

AD-A186 531 HIGH-MOLECULAR COMPOUNDS (SELECTED ARTICLES)(U) FOREIGN 1/1
TECHNOLOGY DIV WRIGHT-PATTERSON AFB OH 14 OCT 87
FTD-ID(RS)T-0553-87

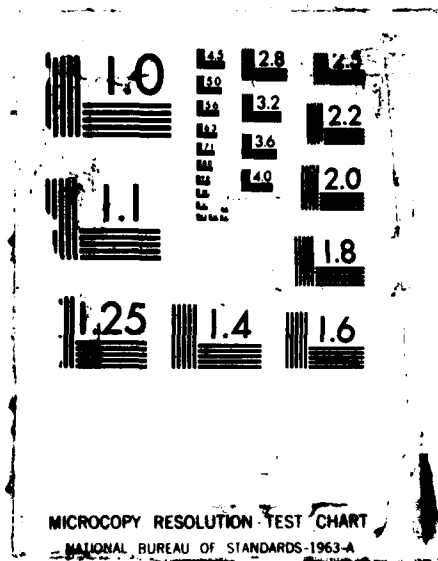
AD-A186 531 HIGH-MOLECULAR COMPOUNDS (SELECTED ARTICLES)(U) FOREIGN 1/1
TECHNOLOGY DIV WRIGHT-PATTERSON AFB OH 14 OCT 87
FTD-ID(RS)T-0553-87

AD-A186 531 HIGH-MOLECULAR COMPOUNDS (SELECTED ARTICLES)(U) FOREIGN 1/1
TECHNOLOGY DIV WRIGHT-PATTERSON AFB OH 14 OCT 87
FTD-ID(RS)T-0553-87

UNCLASSIFIED FID-10(R371-8333-87 F/G 7/6 NL

UNCLASSIFIED FID-10(R371-8333-87 F/G 7/6 NL

UNCLASSIFIED FID-10(R371-8333-87 F/G 7/6 NL



FTD-ID(RS)T-0553-87

AD-A186 531

FOREIGN TECHNOLOGY DIVISION



HIGH-MOLECULAR COMPOUNDS
(Selected Articles)

DTIC
ELECTE
NOV 20 1987
S D



Approved for public release;
Distribution unlimited.



PARTIALLY EDITED MACHINE TRANSLATION

FTD-ID(RS)T-0553-87

14 October 1987

MICROFICHE NR: FTD-87-C-000920

HIGH-MOLECULAR COMPOUNDS (Selected Articles)

English pages: 21

Source: Vysokomolekulyarnyye Soyedineniya, Seriya B,
Kratkiye Soobshcheniya, Vol. 15, Nr. 3, March 1973,
pp. 150-153; 213-216; 222-225

Country of origin: USSR

Translated by: FLS, Inc.

F33657-85-D-2079

Requester: FTD/TQTR

Approved for public release; Distribution unlimited.

| | |
|--------------------|-------------------------------------|
| Accession For | |
| NTIS CRA&I | <input checked="" type="checkbox"/> |
| DTIC TAB | <input type="checkbox"/> |
| Unannounced | <input type="checkbox"/> |
| Justification | |
| By | |
| Distribution/ | |
| Availability Codes | |
| Dist | Adm and/or Special |
| A-1 | |



THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WPAFB, OHIO.

TABLE OF CONTENTS

| | |
|---|----|
| U.S. Board on Geographic Names Transliteration System | 11 |
| The Structure of High Molecular Weight Isotactic Polymethylmethacrylate in Solution, by M.M. Kusakov, A. Yu. Koshevnik, L.I. Mekenitskaya, L.M. Shul'pina, Yu. B. Amerik, L.K. Golova | 1 |
| Study of Optical Anisotropy in Polymethylmethacrylate Stereocomplexes, by M.M. Kusakov, L.I. Mekenitskaya | 8 |
| Naphthalene Breakdown During Naphthalene-Initiated Photo-Sensitized Destruction of Polymethylmethacrylate, by A.V. Kutsenova, V.N. Anisimov, O.N. Karpukhin, V. Ya. Shlyapintokh | 14 |

U. S. BOARD ON GEOGRAPHIC NAMES transliteration SYSTEM

| Block | Italic | Transliteration | Block | Italic | Transliteration |
|-------|------------|-----------------|-------|------------|-----------------|
| А а | <i>А а</i> | A, a | Р р | <i>Р р</i> | R, r |
| Б б | <i>Б б</i> | B, b | С с | <i>С с</i> | S, s |
| В в | <i>В в</i> | V, v | Т т | <i>Т т</i> | T, t |
| Г г | <i>Г г</i> | G, g | У у | <i>У у</i> | U, u |
| Д д | <i>Д д</i> | D, d | Ф ф | <i>Ф ф</i> | F, f |
| Е е | <i>Е е</i> | Ye, ye; E, e* | Х х | <i>Х х</i> | Kh, kh |
| Ж ж | <i>Ж ж</i> | Zh, zh | Ц ц | <i>Ц ц</i> | Ts, ts |
| З з | <i>З з</i> | Z, z | Ч ч | <i>Ч ч</i> | Ch, ch |
| И и | <i>И и</i> | I, i | Ш ш | <i>Ш ш</i> | Sh, sh |
| Й й | <i>Й й</i> | Y, y | Щ щ | <i>Щ щ</i> | Shch, shch |
| К к | <i>К к</i> | K, k | Ъ ъ | <i>Ъ ъ</i> | " |
| Л л | <i>Л л</i> | L, l | Ы ы | <i>Ы ы</i> | Y, y |
| М м | <i>М м</i> | M, m | Ь ь | <i>Ь ь</i> | ' |
| Н н | <i>Н н</i> | N, n | Э э | <i>Э э</i> | E, e |
| О о | <i>О о</i> | O, o | Ю ю | <i>Ю ю</i> | Yu, yu |
| П п | <i>П п</i> | P, p | Я я | <i>Я я</i> | Ya, ya |

*ye initially, after vowels, and after Ъ, Ь; e elsewhere.
When written as ѣ in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

| Russian | English | Russian | English | Russian | English |
|---------|---------|---------|---------|----------|--------------------|
| sin | sin | sh | sinh | arc sh | sinh ⁻¹ |
| cos | cos | ch | cosh | arc ch | cosh ⁻¹ |
| tg | tan | th | tanh | arc th | tanh ⁻¹ |
| ctg | cot | cth | coth | arc cth | coth ⁻¹ |
| sec | sec | sch | sech | arc sch | sech ⁻¹ |
| cosec | csc | csch | csch | arc csch | csch ⁻¹ |

Russian English

rot curl
lg log

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc.
merged into this translation were extracted
from the best quality copy available.

UDC 620.183:541(8+64)

THE STRUCTURE OF HIGH MOLECULAR WEIGHT ISOTACTIC POLYMETHYLMETHACRYLATE
IN SOLUTION

M.M. Kusakov, A.Yu. Koshevnik, L.I. Mekenitskaya, L.M. Shul'pina, Yu.B.
Amerik, L.K. Golova

USSR Academy of Sciences Institute of Petrochemical Synthesis imeni
A.V. Topichev

Submitted 1 June 1971

It was shown in work [1] that the properties of isotactic high
molecular weight polymethylmethacrylate [PMMA] differ from the properties
of isotactic low molecular weight PMMA and we hypothesized that there are
stereocomplexes [2] in a solution of PMMA with a content of 70% isotactic
stereoisomer.

Intending to study the state of high molecular weight isotactic PMMA
in dilute solutions we studied the influence of temperature on their
light refringence, their birefringence in when flowing and their
viscosity

(Russian translation.) ←

The polymer we studied contains almost 100% isotactic stereoisomer, and was obtained by polymerization of methylmethacrylate in toluene at 0° in the presence of PhMgBr [3] and precipitated in a petroleum ether [4]. The content of triads in the polymer obtained, according to NMR data taken on a "Varian-60" instrument was: Isotactic - 96, heterotactic - 3.5, and syndiotactic - 0.5%.

According to data of light spreading in dimethylformamide (DMFA), taken on a FPS-1 instrument by dual extrapolation [5] we determined the molecular weight of the isotactic PMMA. According to measurement results of the dynamic birefringence of solutions in toluene on the instrument described in work [6] and the dynamic viscosity we determined its optical anisotropy. From measurements of the kinetic viscosity at varying rates of shear we determined the characteristic viscosity of the studied polymer in DMFA and in toluene.

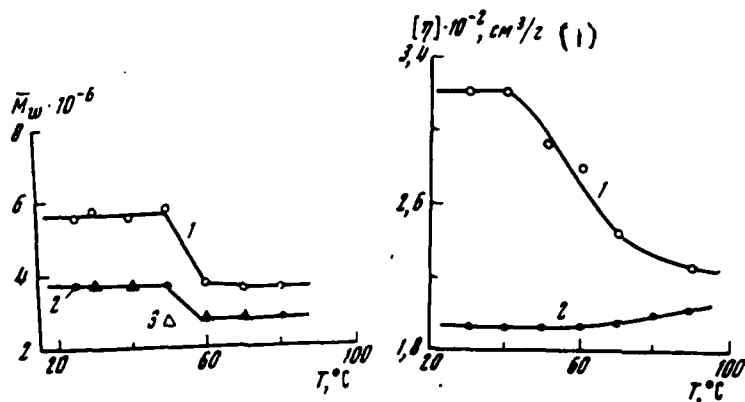
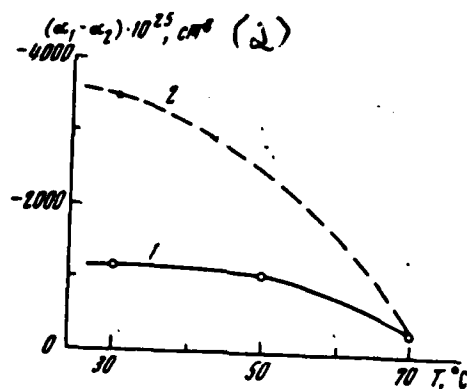


Fig. 1. \bar{M}_w of PMMA as a function of temperature for the first (1), second (2) and third (3) heating cycle.

Fig. 2. $[\eta]$ of PMMA as a function of temperature after the first (1), second (2) and third (3) heating cycle.

Fig. 3. The influence of temperature on the optical anisotropy of PMMA during heating (1), and cooling (2) of its solutions.



Key: (1) $[\eta] \cdot 10^{-2}, \text{cm}^3/\text{g}$
(2) $(\alpha_1 - \alpha_2) \cdot 10^{-2}, \text{cm}^2$

Study of the light spreading was conducted in the temperature range from 30-80° during thrice repeated heating and cooling of the same solution. According to the data obtained for each temperature we calculated the value of the average weight of the molecular mass \overline{M}_w and the second virial coefficient (A_2).

The results of calculations of \overline{M}_w showed (Figure 1) that at -50° there somehow takes place a sharp decrease in molecular weight, although as is known, the molecular weight doesn't have to depend on temperature. As is seen from Figure 1, during the first heating of the solution there is an irreversible decrease in the molecular weight (when the solution is cooled the molecular weight does not return to its former value). During the second and subsequent heating of this same solution there is achieved an reversible value in molecular weight, which decreases during heating to 50° and then regains its former value during cooling.

Parallel changes in the characteristic viscosity (Figure 2) have shown a large change also near to 50°. After repeated secondary heating the characteristic viscosity changes little with temperature, although it does increase somewhat when $T > 60^\circ$.

The results obtained can be explained by the fact that in dilute solutions of high molecular weight, almost completely isotactic PMMA there are associates which fall out near 50°. The character of the changes concerning the molecular weight during the first heating are determined by the inequality of both the initial and the final states.

The inverse value of molecular weight shows the existence of associated which fall out at about 50° and are formed again during cooling. We must also note here that the second Virial coefficient (A_2) remains practically at zero at all temperatures.

Characteristic viscosity and optical anisotropy of isotactic PMMA in a solution with toluene at 30°

| Content, % | $[\eta] \cdot 10^{-242}$, cm^3/g | Derived anisotropy $[\eta]/[\eta] \cdot 10^{-10}$ $\text{cm} \cdot \text{sec}^2/\text{g}$ | Segmental anisotropy $(\alpha_1 - \alpha_2) \cdot 10^{-25}$ cm^3 |
|------------|--|---|---|
| 96 | 1.35 | -97 | -1200 |
| 96 | 2.60 | -87 | -1100 |
| 70 | 1.60 | -30 | -375 |
| 70 | 1.80 | -34 | -425 |

Association of PMMA macromolecules can be expressed by the cooperative interaction of the polar ethers of the groups which are regularly situated along the chain of the isotactic macromolecules, and which exist in spiral conformation. The high level of cooperation of this interaction is provided for by a quite high value of molecular weight.

The optical anisotropy of the studied isotactic PMMA (the Table) was very high in absolute value and inverse in sign. This result shows the very organized structure of the macromolecule in solution and also can go to show the existence of secondary structure. From the table where we have presented also the values for optical anisotropy of two forms of high molecular weight isotactic PMMA containing 70% of the stereoisomer, it is seen that when the content of the isotactic link is increased the absolute value of anisotropy increases and when there are high values for the molecular weight, it maintains an almost constant value.

Adding to the conclusion about the regularized structure of the high molecular weight isotactic PMMA are the authors of work [7], in which is expressed a hypothesis that when there is an increase in molecular weight beginning with any value, the "disorder" leads to "order."

Regularity in the structure of high molecular weight isotactic PMMA evidently is a result of low mobility of the side groups. This concept is confirmed by experimental results obtained in work [8].

The correlation of some physical properties of isotactic stereoisomer PMMA in the solid state or as gels [7-9], with anisotropy of its macromolecules in dilute solutions allows us to think that even in solution the macromolecules have properties which allow organization of structure in the solid state.

Study of the influence of temperature on the value of optical anisotropy of high molecular weight isotactic stereoisomer showed (Figure 3) that when heated to 50°, the value of anisotropy is practically unchanged; further increase in temperature leads to a decrease in it, which shows that there is partial breakdown in the regularity of structure. After subsequent cooling of the solutions to their initial temperature, as is seen in Figure 3, there is a significant resumption of the absolute value of anisotropy. Such a change in anisotropy, which causes an increase in the level of regularity of structure, can be attributed, evidently, to the transformation of the macromolecule from one conformation to another. The question of the existence of two confirmations of isotactic PMMA -5₁ and 5₂- has already been discussed in the literature, coming from data of x-ray analysis of films, from study of the absorption spectra of the solutions in the near UV area, and also by conformational analysis data [10-12]. It is quite certain that the conformational transform takes place at a temperature which provides for a sufficiently high internal mobility of the isotactic chains (55-60° [9]).

Conclusions

1. In dilute solutions of high molecular weight, almost completely isotactic polymethylmethacrylate (PMMA) there are persistent associates present in the macromolecules with an organized secondary structure.

2. Associates of PMMA break down at a temperature of around 50° and the form again when the substance is cooled to room temperature.

3. When the solutions of high molecular weight isotactic stereoisomer which have preliminarily heated to 50° are cooled, there is a change in the optical anisotropy, which characterized the further regularity of structure of the macromolecules of this stereoisomer.

LITERATURE

1. A.Yu. Koshevnik, M.M. Kusakov, N.M. Lubman, L.I. Mekenitskaya, O.V. Orlova, A.A. Pasynskaya, E.A. Razumovskaya, L.M. Shulpina, *Vysokomolekulyarnyye soyedineniya*, Vol. A12, 1970, p. 2103.
2. A.M. Liquori, G. Anzuino, V. Coiro, M.D. Alagni, P. DeSantis, M. Savino, *Nature*, Vol. 206, 1965, p. 358.
3. Tsunco Kodama, Fumio Ide, Kazuo Nakazuca, *Chem. High Polymer*, Vol. 22, 1965, p. 225.
4. F.A. Bovey, *J. Polymer Sci.*, Vol 44, 1960, p. 59.
5. V.N. Tsvetkov, V.Ye. Eskin, S.Ya. Frenkel, *Struktura makromolekul v rastvorakh* (Structure of Macromolecules in Solution), "Nauka," 1964.
6. M.M. Kusakov, N.M. Lubman, L.I. Mekenitskaya, *Pribory i tekhnika eksperimenta* (Instruments and Experimental Equipment), Vol. 5, 1967, p. 221.
7. C. Ryan, P. Flescher, *J. Phys. Chem.*, Vol. 69, 1965, p. 3384.
8. M. Shindo, I. Muracami, *Chem High Polymer*, Vol. 26, 1969, p. 358.
9. H. Shindo, I. Muracami, H. Yamamura, *J. Polymer Sci.*, Vol. 7, Nr. A-1, 1969, p. 297.
10. V.MN. Coiro, P. deSantis, A.M. Liquori, M. ~~M~~azzarella, *Symposion of Macromolecular Chemistry*, Praga, 1965.
11. M. D'Alagni, P. deSantis, A.M. Liquori, M. Savino, *J. Polymer Sci.*, Vol. B2, 1964, p. 921.
12. F.P. Grigoryeva, T.M. Birshteyn, Yu.Ya. Gotliv, *Vysokomolekulyarnyye soyedineniya*, Vol. A9, 1967, p. 580.

UDC 541.64:535.012

STUDY OF OPTICAL ANISOTROPY IN POLYMETHYLMETHACRYLATE STEREOCOMPLEXES

M.M. Kusakov, L.I. Mekenitskaya

USSR Academy of Sciences Institute of Petrochemical Synthesis imeni A.V.
Topichev

Submitted: 9 July 1971

In works [1,2] it was shown that stereocomplexes of polymethylmethacrylate (PMMA) are formed in some solvents when they are mixed into solutions of PMMA of various microstructure (syndio- and isotactic), they have high molecular weight, the value of which depends on the relative concentration in the syndio- and iso- component complexes.

In this article we present the results of study of optical anisotropy of stereocomplexes which characterize the orderliness of their structure, at various concentrations in complex source stereoisomers.

Optical anisotropy is determined according to the results of measurement of the birefringence in a stream on the instrument described in [3], and the dynamic viscosity of the solutions. Intent of determining the characteristics of the anisotropy itself of the complexes and of excluding the effect of form [4], we opted to use toluene as our solvent, because its refractive index is near to the refractive index of the polymer.

We selected two forms of high molecular weight PMMA to use as the isotactic stereoisomer [5]: The first had average molecular weight of $\overline{M}_w=2.7 \cdot 10^6$ and level of stereoregularity of 70%, and the second had $\overline{M}_w=5.5 \cdot 10^6$ and level of stereoregularity of 96%. As a syndiotactic stereoisomer we used a low molecular weight sample [5] with $\overline{M}_w=0.04 \cdot 10^6$ and level of stereoregularity at 80%.

The PMMA complexes were obtained by mixing dilute solutions of iso- and syndiotactic PMMA of identical concentration¹ ($c=0.15$ g/dl) at varying component ratios.

Presented in figure one is the segmental anisotropy of the stereocomplexes as a function of their makeup. The obtained values for anisotropy that we obtained are very large in absolute value and are negative in sign, attesting to the fact the stereocomplexes are rigid ordered structures and that their regularity depends on the relative concentration of stereo- and isotactic forms of PMMA. The maximum of the absolute value of anisotropy, observed for a complex with ratio of syndio- to isocomponents of 1:1 shows the maximum regularity of the structure of a complex with such a makeup. The maximum molecular weight of the complexes, as we showed earlier [1,5] corresponds to a component

¹. As was established in [5], for dilute solutions of complexes of mixture the deduced anisotropy does not depend on the initial concentration at which the mixing takes place.

ratio of 2:1. This same component ratio was measured during study of the birefringence of solutions of complexes with minimal limiting angle of orientation (Figure 2), since in the stream the heavier particles are more oriented than the light ones. This leads us to conclude that the heaviest particles of the complex are not the most regular. From Figure 1 is seen that anisotropy of the complexes obtained based on isotactic PMMA containing 70% stereoisomer are virtually the same as those based almost completely on the isotactic stereoisomer.

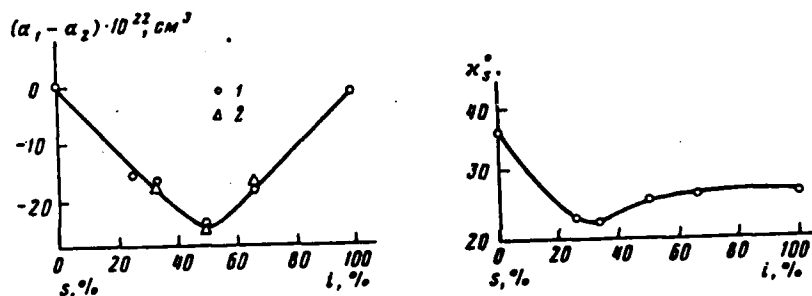


Figure 1. Segmental anisotropy ($\alpha_1 - \alpha_2$) of stereocomplexes obtained by mixing solutions of syndio- and isotactic PMMA as a function of the makeup of (iso- and syndiotactic PMMA) for samples of isotactic PMMA containing 96 (1) and 70% (2) stereoisomer.

Figure

2. The limiting angle of orientation χ_s° of stereocomplex as a function of their makeup.

Study of the influence of temperature on the optical anisotropy of the complexes of various makeup has shown (Figure 3a) that stability of the structure of the complexes depends both on temperature and on their makeup. When heated to 50°, the structure of the complexes changes

little at all ratios of syndio- and isocomponents, but there is a tendency noted to breakdown in complexes with relatively small concentrations of syndiocomponent.

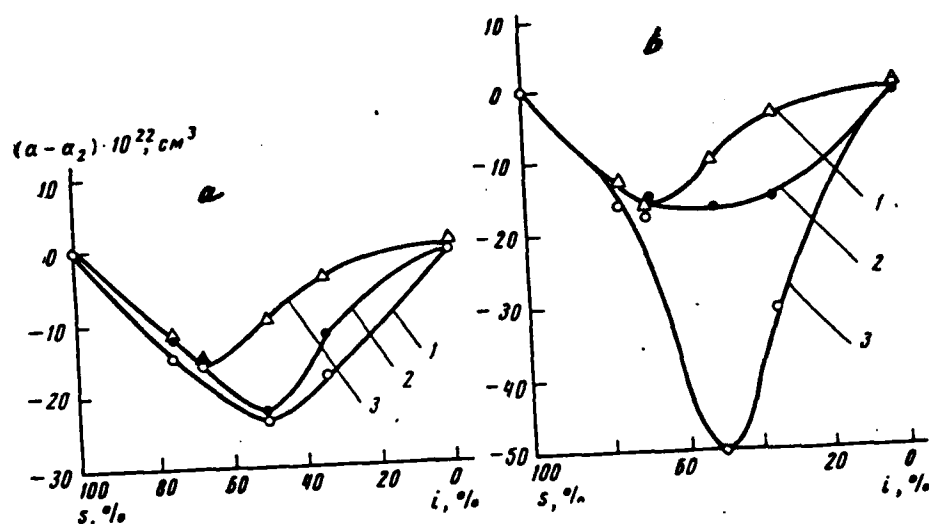


Figure 3. The influence of temperature on the anisotropy of complexes when heated (a) 1- 30; 2 - 50; and 3 - 70° and cooling (b) 1- 70, 2 - 50, and 3 - 30°

In the temperature range of 50-70° there is observed a sharply expressed breakdown in the structure of complexes with high concentration of syndiotactic chains. Only those complexes in which on one isotactic macromolecule there are two or more syndiotactic macromolecules, which are practicable stable at 70 and even at 80° (complex with ratio of syndio:iso = 2:1 heated to 80°). The data obtained strongly confirm Liquori's hypothesis [2] of the structural model of the stereocomplexes, in accordance with which the syndiotactic macromolecules are somehow acting as armor for a series of isotactic chains, which are in a spiral conformation.

When the solutions are gradually cooled to their initial temperature (Figure 3b) it turns out that those complexes whose structure is stable when heated even to 70-80°, are changed little in structure even when they are later cooled to their initial temperature of 30°. For the complexes, whose anisotropy at 70° is decreased, cooling to the source temperature leads to a significant increase in the absolute value of anisotropy, achieving a maximum also at a syndio:iso ratio of 1:1. Such a change in anisotropy influences further regularity of the structure of the complexes and is caused, evidently, by the conformational transformations which take place during heating in the chains of the high molecular weight isotactic stereoisomer, which is part of the makeup of the complex.

Conclusions

1. Stereocomplexes of polymethylmethacrylate (PMMA) form in dilute solutions into organized structures, the level of regularity of which depends on the relative content of syndio- and isocomponents. The maximum regularity in structure is seen in a complex with component ratio of syndio:iso = 1:1.
2. The stability of the structure of complexes depends on temperature and on makeup.
3. We observed an irreversible change in the optical anisotropy of the complexes, accompanying an increase in temperature and characterizing a further growth in the structure's regularity.

LITERATURE

1. A.M. Liquori, G. Anzuino, V.M. Coiro, M. D'Alagni, P. deSantis, M. Savino, *Nature*, Vol. 206, 1965, p. 358
2. A.M. Liquori, M. deSantis, M. Savino, M. D'Alagni, *J. Polymer Sci.*, Vol. B4, 1966, p. 943
3. M.M. Kusakov, N.M. Lubman, L.I. Mekenitskaya, *Pribory i tekhnika eksperimentov* (Instruments and Experimental Equipment), Vol. 5, 1967, p. 221.
4. V.N. Tsvetkov, V.Ye. Eskin, S.Ya. Frenkel, *Struktura makromolekul v rastvorakh* (Structure of Macromolecules in Solution), "Nauka," 1964.
5. A.Yu. Koshevnik, M.M. Kusakov, N.M. Lubman, L.I. Mekenitskaya, O.V. Orlova, A.A. Pasynskaya, E.A. Razumovskaya, L.M. Shulpina, *Vysokomolekulyarnyye soyedineniya*, Vol. A12, 1970, 2103.

UDC 541.64:547.652.1

NAPHTHALINE BREAKDOWN DURING NAPHTHALINE-INITIATED PHOTO-SENSITIZED
DESTRUCTION OF POLYMETHYLMETHACRYLATE

A.V. Kutsenova, V.N. Anisimov, O.N. Karpukhin, V.Ya. Shlyapintokh
USSR Academy of Sciences Institute of Chemical Physics

Submitted: 12 July 1971

In works [1,2] it was shown that naphthalene is a photosensitizer of chemical transformations in polymethylmethacrylate (PMMA), but the mechanism of photodestruction is quite complex. According to data [1,2], accumulation of free radicals and destruction of the macromolecule take place as a result of absorption of a second quantum of light by the naphthalene molecule in a triplet state. Along with this, consumption of naphthalene takes place using a single quantum mechanism. While studying photosensitized transformation of PMMA, we discovered an interesting peculiarity of the latter reaction, which is that extinguishing the fluorescence of naphthalene does not lead to a slowing in its consumption. This phenomenon is examined in this work.

Experimental Methodology

The object of research was PMMA, prepared by the "Orgsteklo" Combine, with a molecular weight of 160,000; monomer content of ~1% (the concentration of which was established by UV-spectrum absorption [3]). Chemically pure naphthalene was supplementarily purified by sublimation.

Films 5-10 μm thick were prepared from solution in methylene chloride. The naphthalene concentration was determined by UV and IR spectra [4]. The products which accumulated during the course of the photosensitized transformation, absorbed light in the very part of the spectrum as naphthalene. To determine the naphthalene concentration during the course of the photo-process we measured the optical density of the film in the area of 260-280 nm. In this area the absorption spectrum of the products was a monotonous unstructured band, which in the area under observation could approximate a linear function. In connection with this, to determine the naphthalene concentration $[H]$, we could use the methodology [5], in accordance with which

$$[H] \sim \frac{\lambda_1 - \lambda_0}{\lambda_2 - \lambda_0} (D_1 - D_0) + (D_2 - D_0),$$

where λ_1 and D_1 are the wave length and corresponding optical density. Measurement was done at wavelength $\lambda_0=271$, $\lambda_1=267$, and $\lambda_2=277$ nm. The naphthalene concentration, determined by IR and UV spectras was in substantial agreement (Figure 1). The Lambert-Beer law for the source film was fulfilled right up to naphthalene concentration of 5% by weight. the UV spectrum of naphthalene in the concentration range of 0.05-5% also remained unchanged. Naphthalene which vaporized out of the film which had been heated to 80° amounted to 10-15% over 15-20 hours, that is for the time of illumination (6-8 hours) conducted at room temperature any evaporation of naphthalene was negligible.

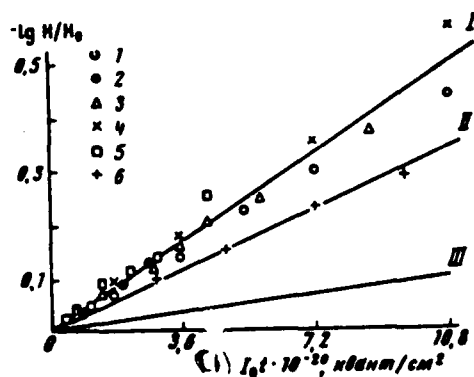


Figure 1. Semilog function of the relative concentration of naphthalene to the illumination dose in the UV (1-3,5,6) and IR spectras (4) when $I_0 \cdot 10^{-16} = 20$ (1,5); 2.5 (2); 4 (3,5,6) quanta $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ (6 with the addition of 4.4% by weight of Tinuvin II); $[H] = 5\%$.
Key: (1) $I_0 t \cdot 10^{-20}$ quanta/cm 2

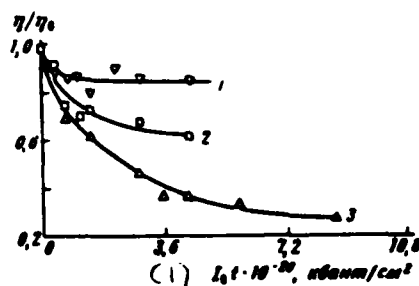


Figure 2. Changes in the relative yield of fluorescence η/η_0 from the dose of illumination at $I_0 = 4.0 \cdot 10^{16}$ quanta $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. Naphthalene concentration was 0.05 (1), 0.5 (2), and 5% by weight (3).
Key: (1) $I_0 t \cdot 10^{-20}$ quanta/cm 2

Illumination was done in air using a DRSh-1000 or DRSh-250 mercury lamp and a BS-4 light filter which passed light $\lambda > 290$ nm, and not absorbed by the polymer. The absolute intensity of the light falling on the samples was measured using a Ferrosilicate actinometer and was controlled by a photoelement.

We excited the naphthalene to luminescence using light of 304 nm, separated from the spectrum of the DRSh-250 mercury lamp using a DMR-4

monochromator and registered using a SF-4 monochromator with a FEU-38 photo multiplier at the output.

File thickness in all tests was set up in such a way that the sample absorbed no more than 10% of the photochemically active light, which allowed us to consider the intensity of light within the sample to be equal.

The kinetics of breakdown of the ether groups in the PMMA were studied through changes in the IR-spectra in the area of $1200-1300\text{ cm}^{-1}$ [6].

Results and Their Evaluation

Kinetics of phototransformation of naphthalene. Semilogarithmic anamorphoses of the relative concentration of naphthalene as a function of the dose of illumination ($I_0 t$, where I_0 is the intensity of the incident light) at various initial concentrations of naphthalene (from 0.5 to 5% by weight) and the intensity of the light were altered by a factor of eight (Figure 1, curve 1), and were presented on a single direct line. This means that naphthalene is expended at a rate that is proportional to the amount of light they absorb over the course of the entire time of illumination. According to the accompanying evaluation the quantum yield for naphthalene expenditure was $0.9 \cdot 10^3$.

During the course of the photoprocess the intensity of the fluorescence of naphthalene decreased gradually. The kinetic curves of the change in relative quantum yield of fluorescence at various initial concentrations of naphthalene (Figure 2) show that if there are large initial concentration of naphthalene, the quantum yield of fluorescence decreases by a factor of two to four, which is apparently connected with extinguishing of the action of the reaction products. At the same time,

as seen from Figure 1, the quantum yield of naphthaline during the course of the reaction does not change. This shows that the photosensitizer - naphthaline - is broken down in the process, the rate of which is not determined by the concentration of the same particles which are responsible for fluorescence. This conclusion supports the analysis of the data concerning the consumption of naphthaline in the presence of a light stabilizer, Tinuvin II ($2.3 \cdot 10^{-2}$ moles/liter), as presented in Figure 1. Suppression of the fluorescence and absorption of the light by the Tinuvin II will decrease the rate of naphthaline consumption by a factor of five (curve III). There was also experimental observation of the decrease by a factor of merely 1.5, which can be explained, considering only the filtration of light by the Tinuvin II (curve II).

Considering the small quantum yield of the chemical transformation, one may hypothesize that in order for the reaction to proceed there must be either a supply of quantum energy obtained by the molecule during absorption of a quantum of light, or there is a relatively rarely encountered mutual disposition of molecules among the sensitizer also.

If there is a second of these hypothesized mechanisms, we must consider that the number of naphthaline molecules located in a suitable place for the reaction do not change over time, since there is no change in the course of the process of the quantum yield of naphthaline consumption. It follows the equilibrium of the location of the naphthaline molecule relative to the matrix molecule can be established over time for a time $\tau < \Delta t$, where Δt is the average time between absorptions of a photon by a given naphthaline molecule. Under the conditions of our tests, Δt was about one second.

Photosensitized breakdown of the polymer's ether groups. According to changes in the optical density of the absorption band in the IR spectrum of ^{PMMA} _A with the use of the methodology in [6], we conducted

measurements of the rate w_{ROR} of the breakdown of ether groups. Illumination was done in the absorption band for naphthaline. This showed that the value of w_{ROR} is unequivocally determined by the amount of light which is absorbed by the naphthaline. The quenching of the fluorescence of naphthaline has no influence on the rate of the ether group breakdown process or on the rate of naphthaline consumption. This allows us to put forth the hypothesis that the ether groups and the naphthaline are transformed in one and the same process which is in agreement with the close values of the quantum yields of ether group breakdown -- $\Phi_{\text{ROR}} = 1.7 \cdot 10^{-3}$ and naphthaline transformation - $\Phi = 0.9 \cdot 10^{-3}$.

We must note that we observed stereospecificity in the photosensitizing reaction of ether group breakdown. During direct photolysis of PMMA the rate for decrease of the optical density in the area of 1270 cm^{-1} , corresponding to syndioform, was 1.3 times greater than the rate of decrease for the optical density in the area of 1250 cm^{-1} which described the isoform of PMMA [6]. But during a photosensitized reaction the optical density in the area of 1270 cm^{-1} is practically unchanged. The only groups that break down are those which have an absorption band at 1250 cm^{-1} (isoform) and at 1190 cm^{-1} (the oscillation of the ether skeleton of the iso- and syndioform with addition of deformational oscillations by C-H [7]). Furthermore, the relationship between the quantum yield of breakdown of the ether group and the breakdowns in the photosensitized reaction (the quantum yield of breakdowns was evaluated by data in [1]) was 10-15, while during direct photolysis it was ~ 100 [6]. These facts show that the worth of the process of photosensitized destruction over direct photolysis.

When selecting a light stabilizer one must consider that the photosensitizing of PMMA transformation by naphthaline takes place as an irreversible reaction which apparently one cannot stop by extinguishers of the excited state.

Conclusions

1. We showed that extinguishing of the fluorescence of naphthaline does not lead to slowdown in the rate of its consumption.

2. During photosensitized destruction of polymethylmethacrylate using naphthaline, there is stereospecificity in the breakdown of the ether groups of the polymer and there is a changing relationship between the quantum yields during the progress of the various processes.

LITERATURE

1. I.G. Batekha, Yu.B. Shekk, S.A. Krysanov, M.V. Alfimov, Dokl AN, Vol. 197, 1971, p. 614.
2. V.G. Vinogradova, B.I. Shelimov, N.V. Fok, Khimiya vysokikh energii, Vol. 2, 1968, p. 136.
3. M. Warnock, P. Gardner, J. Appl Polymer Sci., Vol. 12, 1968, p. 2325.
4. G.C. Pimental, A.L. McClellan, J. Chem. Phys., Vol. 20, 1952, p. 270.
5. A. Gillem, Ye. Shtern, Elektronnyye spektry poglosheniya organicheskikh soedinenii (Electron Absorption Spectra for Organic Compounds), Izdatelstvo inostrannykh literature, 1957, p. 253.
6. V.I. Golderberg, Dissertation, 1971.
7. H. Nagai, J. Appl. Polymer Sci., Vol 7, 1963, p. 1697

DISTRIBUTION LIST
DISTRIBUTION DIRECT TO RECIPIENT

| <u>ORGANIZATION</u> | <u>MICROFICHE</u> |
|------------------------|-------------------|
| A205 DMAHTC | 1 |
| A210 DMAAC | 1 |
| B344 DIA/RTS-2C | 9 |
| C043 USAMIA | 1 |
| C500 TRADOC | 1 |
| C509 BALLISTIC RES LAB | 1 |
| C510 R&T LABS/AVRADCOM | 1 |
| C513 AVRADCOM | 1 |
| C535 AVRADCOM/TSARCOM | 1 |
| C539 TRASANA | 1 |
| C591 FSTC | 4 |
| C619 MIA REDSTONE | 1 |
| D008 NISC | 1 |
| E053 HQ USAF/INET | 1 |
| E404 AEDC/DOF | 1 |
| E408 AFWL | 1 |
| E410 AD/IND | 1 |
| E429 SD/IND | 1 |
| P005 DOE/ISA/DOE | 1 |
| P050 CIA/OCR/ADD/SD | 2 |
| AFIT/LDE | 1 |
| FTD | |
| CCN | |
| NIA/PHS | 1 |
| LLNL/Code L-389 | 1 |
| NASA/NST-44 | 1 |
| NSA/1213/TDL | 2 |
| ASD/FTD/1Q1A | 1 |

END
DATE
FILMED
JAN
1988